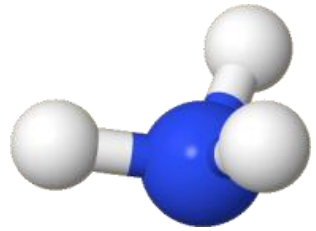
Universität Bremen

Institute for Applied and Physical Chemistry

Faculty 02
Biology/Chemistry

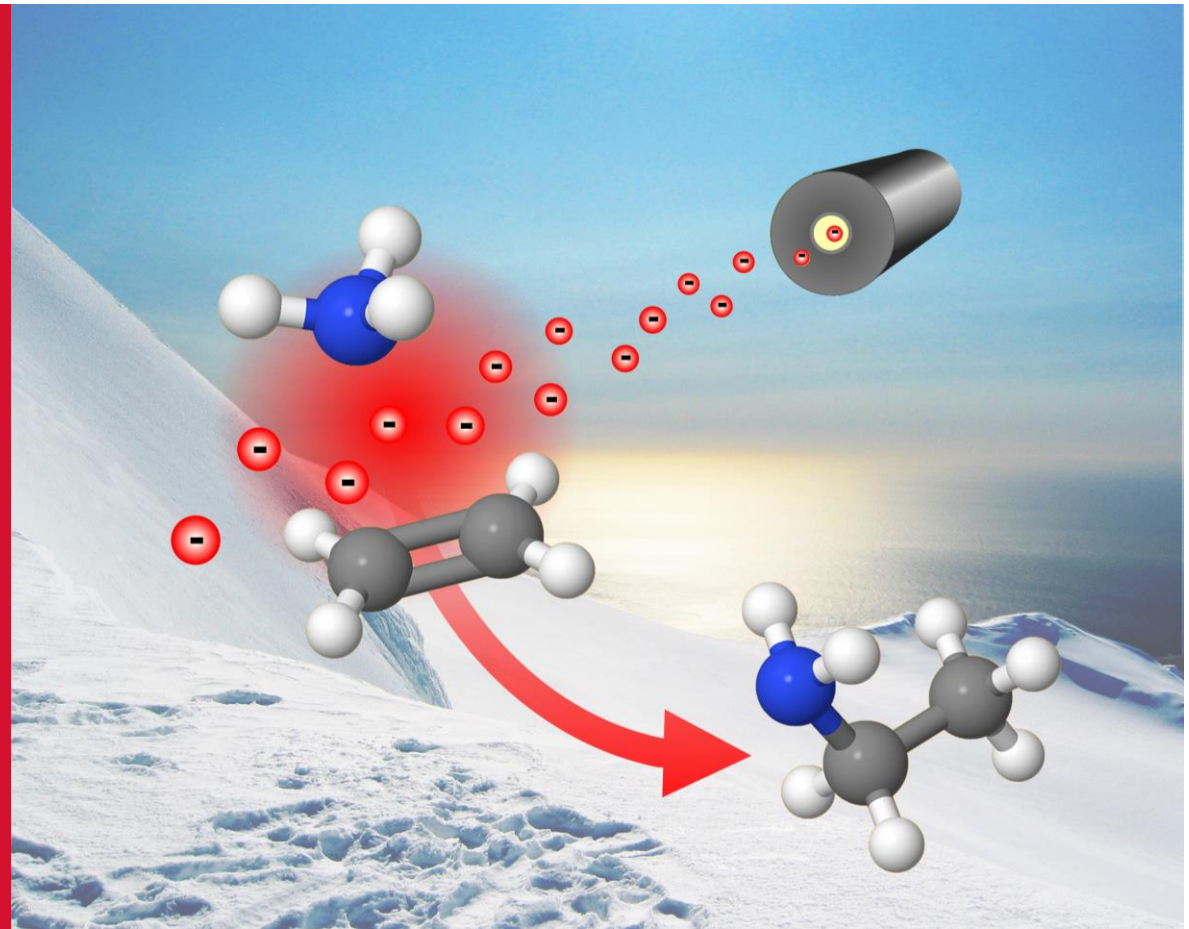
Electron-induced chemistry in Bremen

From fundamentals to astrochemistry and nanofabrication



Petra Swiderek
Jan Hendrik Bredehöft

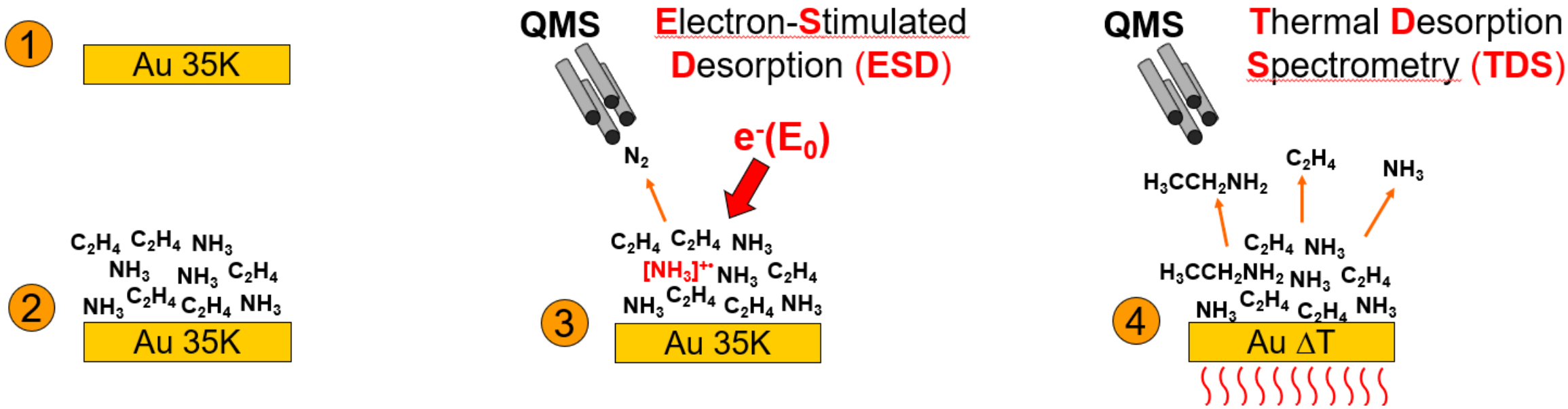
iAPC



Electron-induced chemical synthesis

- Reaction mechanisms
- Astrochemistry
- Modification of materials
- Surface functionalization

Desorption experiments



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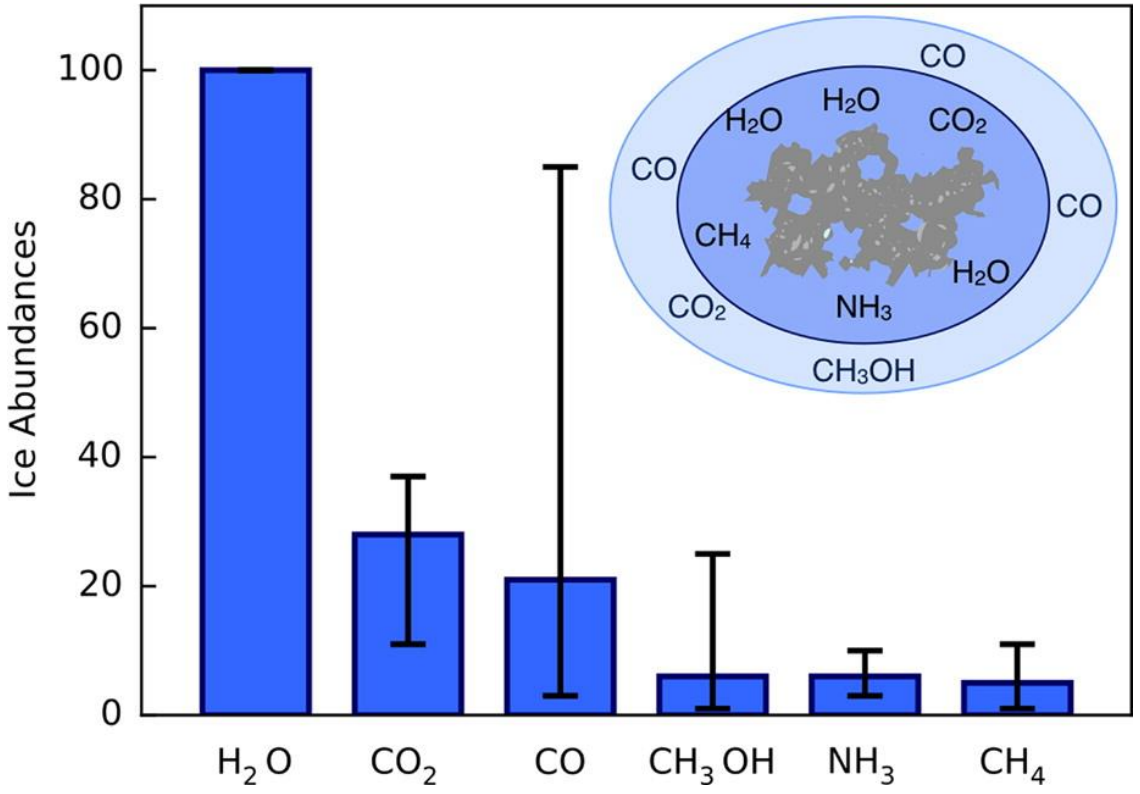
IAPC

LEE-driven chemistry in interstellar ices



K.I. Öberg, *Chem. Rev.* **116**, 9631 (2016).

- Ices of small molecules form on dust grains.
- Low-energy secondary electrons released upon impact of cosmic radiation drive chemical reactions.

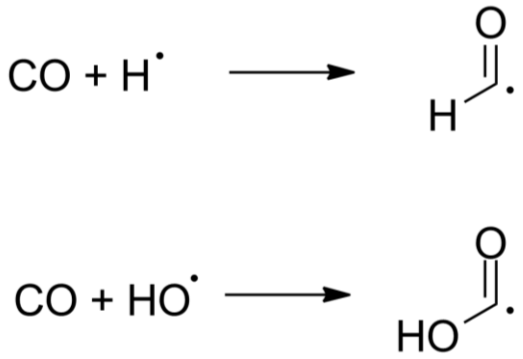
- Case study:

  Reactions between H_2O and CO

F. Schmidt, P. Swiderek, **J. H. Bredehöft**,
ACS Earth Space Chem. **3**, 1974-1986 (2019).

LEE-driven chemistry in mixed $CO:H_2O$ ice

Previous view of reaction mechanism:



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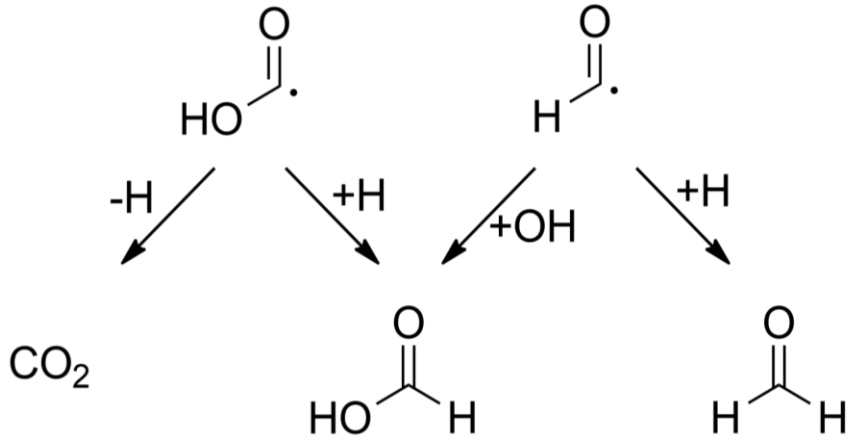

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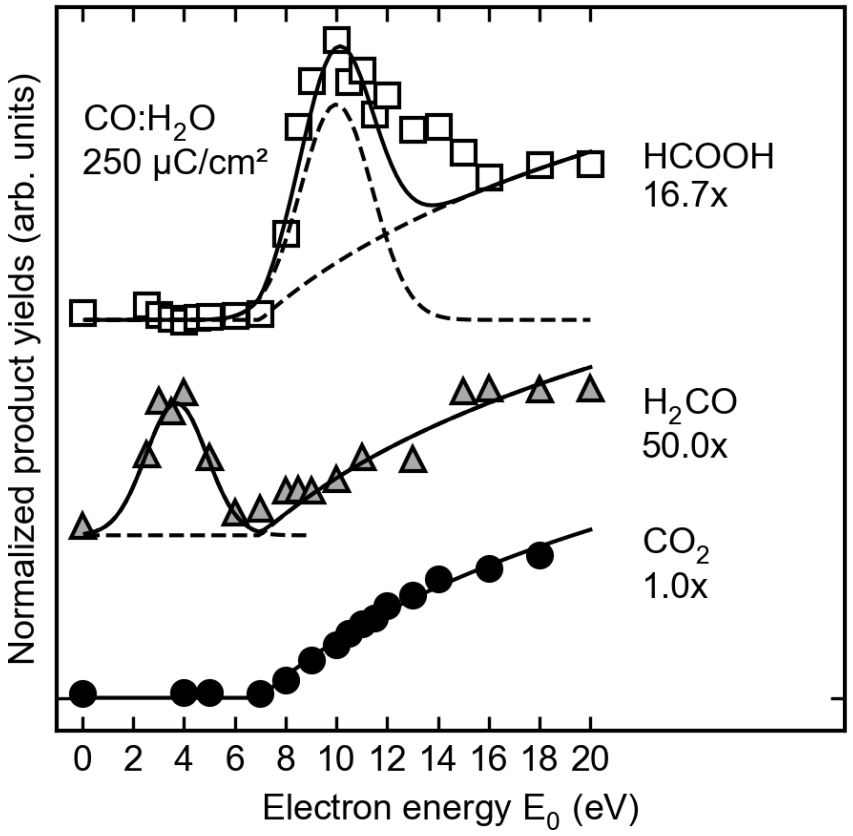

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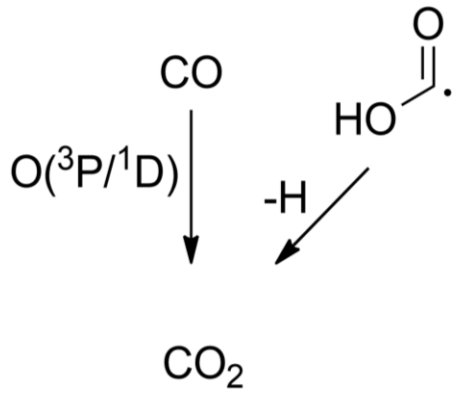
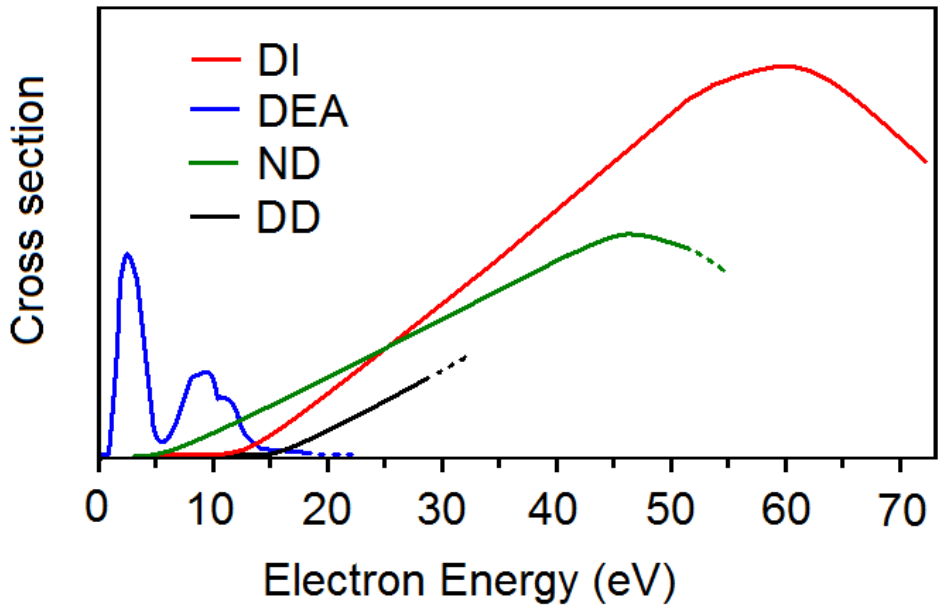


???

F. Schmidt, P. Swiderek, J. H. Bredehöft,
ACS Earth Space Chem. **3**, 1974-1986 (2019).

Initial electron-molecule interactions



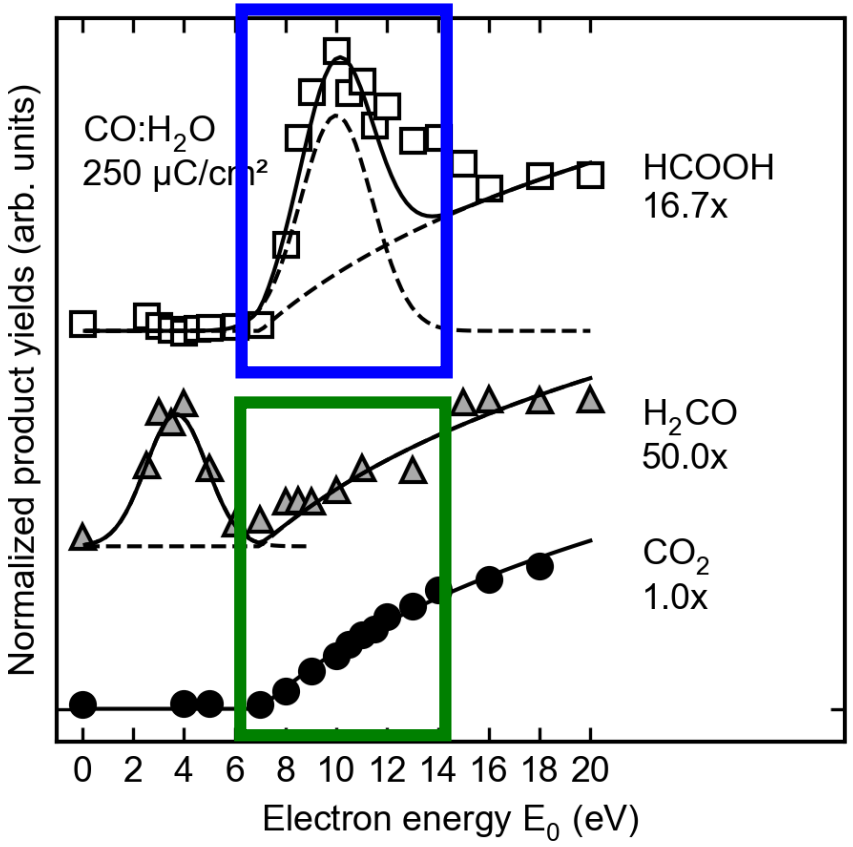
Electron **I**onization / **D**issociative **I**onisation

Electronic **E**xcitation / **N**eutral **D**issociation

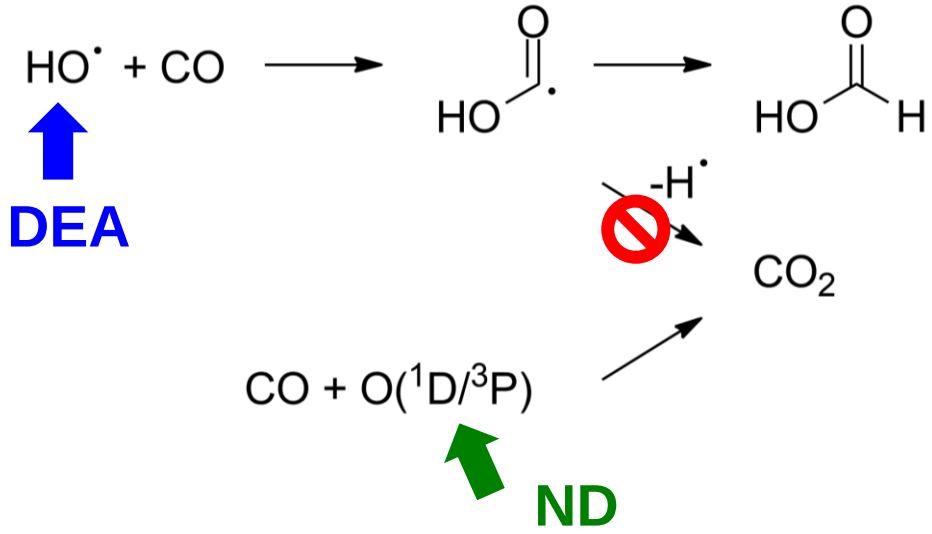
Electron **A**ttachment /
Dissociative **E**lectron **A**ttachment

E.Böhler, J. Warneke, P. Swiderek,
Chem. Soc. Rev. **42**, 9219 (2013).

LEE-driven chemistry in mixed $CO:H_2O$ ice



Loss of H from HOCO is not the dominant mechanism:



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Electron-induced synthesis

Open Access Review

Mechanisms of Electron-Induced Chemistry in Molecular Ices

by Fabian Schmidt, Tobias Borrmann, Martin Philipp Mues, Sanna Benter, Petra Swiderek and Jan Hendrik Bredehöft *

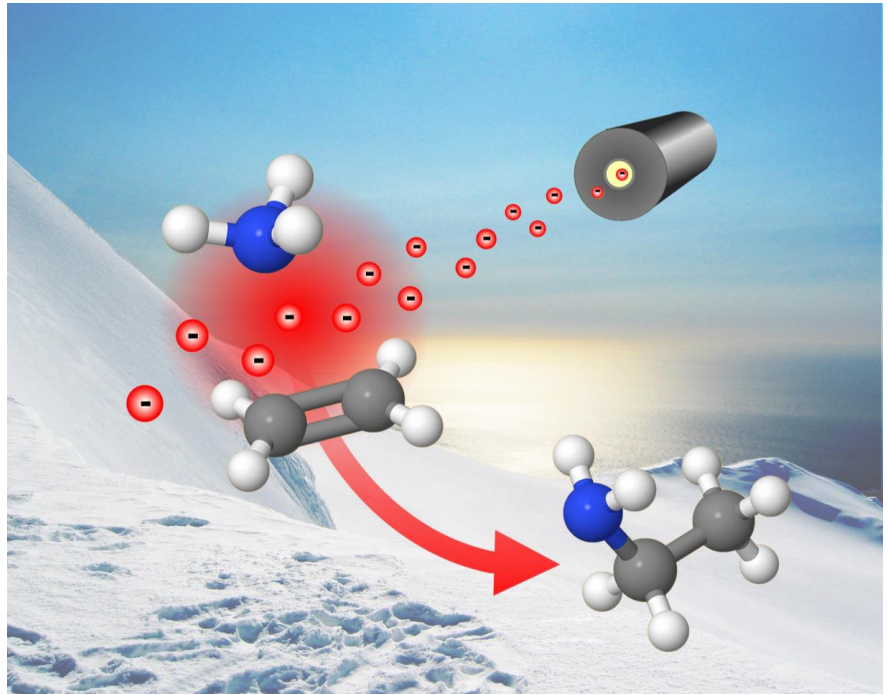
Institute for Applied and Physical Chemistry, University of Bremen, Leobener Straße 5, 28359 Bremen, Germany

* Author to whom correspondence should be addressed.

Atoms **2022**, *10*(1), 25; **https://doi.org/10.3390/atoms10010025**

Electron-induced reactions for modification of materials

- Nitrogen incorporation in carbonaceous FEBID materials



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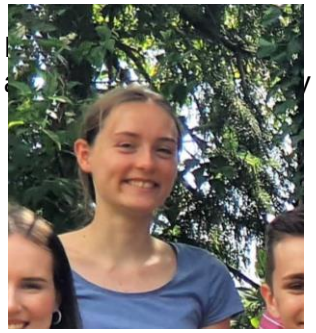
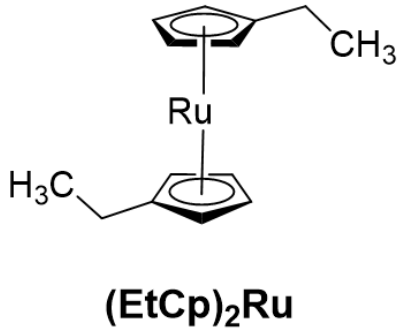
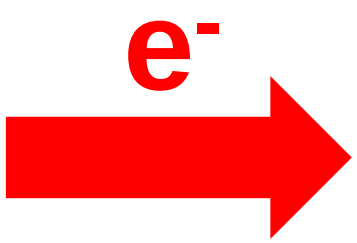


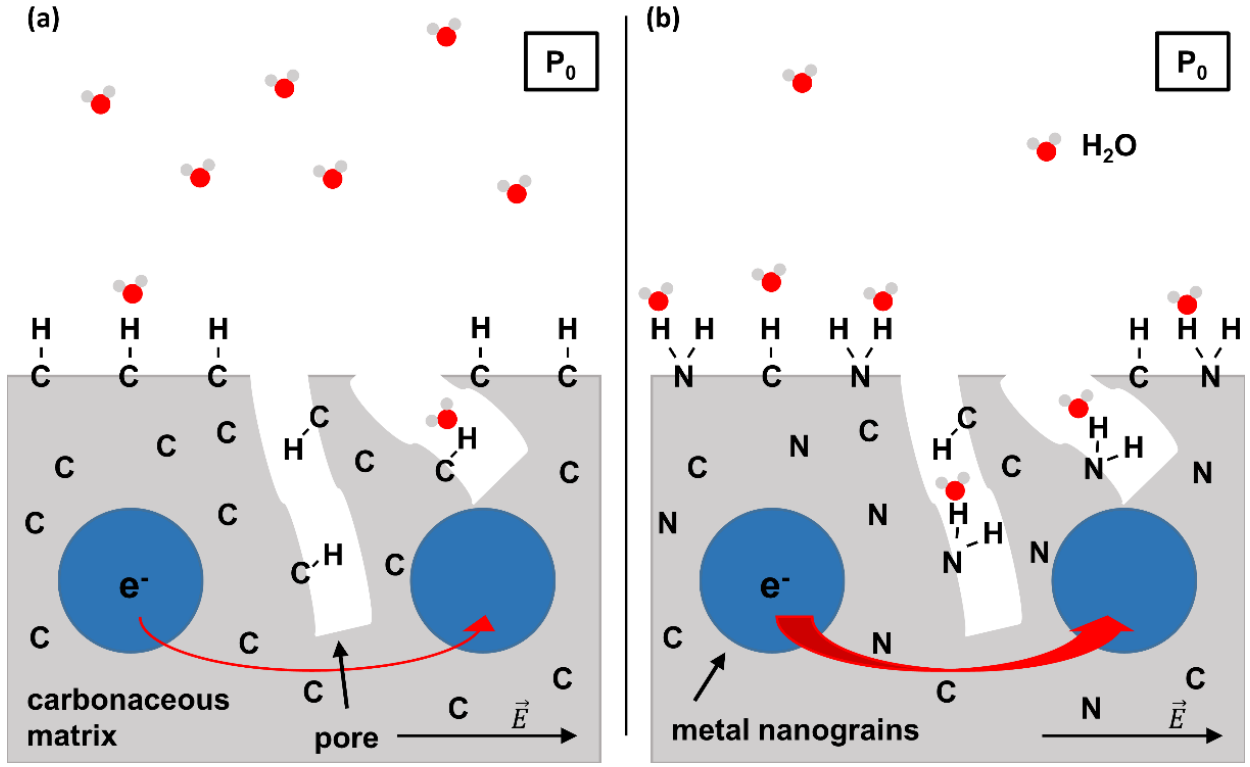
Carbonaceous materials for humidity sensing

- Integration of nitrogen into carbonaceous deposit enhances binding of H_2O.



$(EtCp)_2Ru$

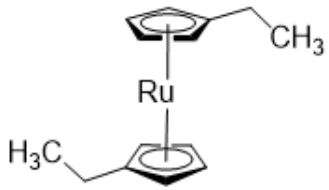




H. Boeckers, P. Swiderek, M. Rohdenburg, *Nanomaterials* **12**, 4455 (2022).

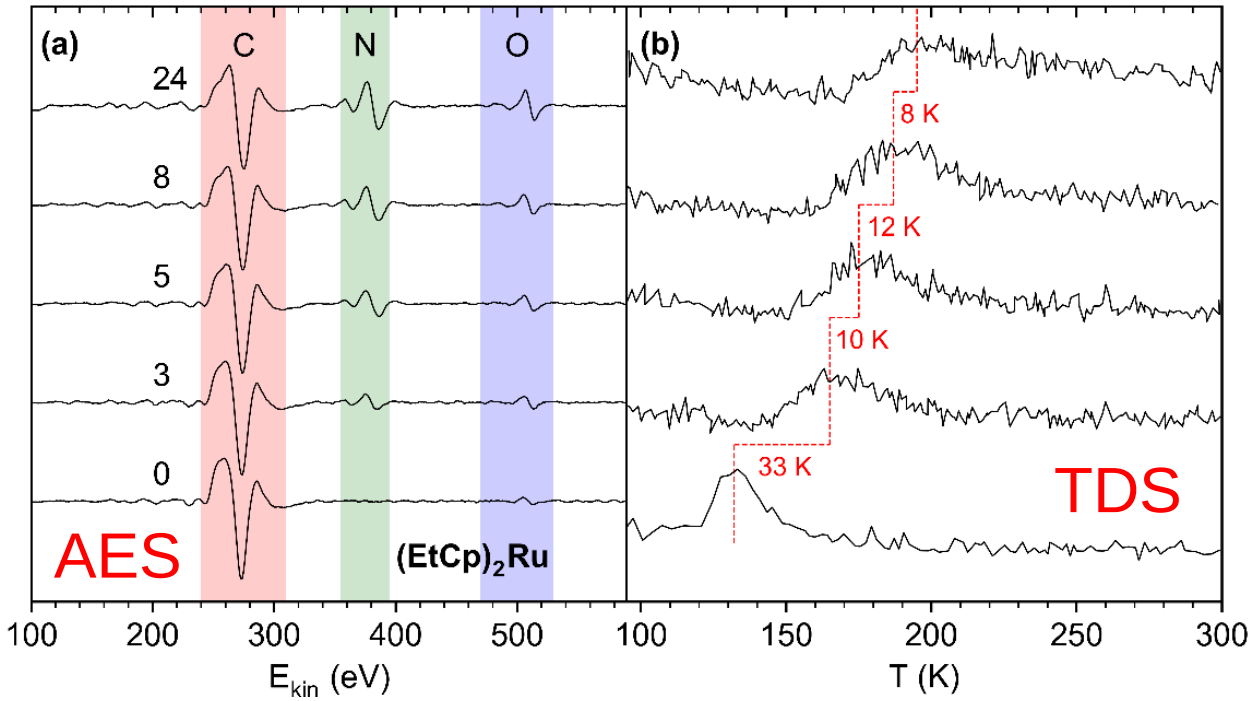
Tuning the binding of H_2O

- Cycles of NH_3 adsorption and electron irradiation onto deposit.
- **A**uger **E**lectron **S**pectroscopy shows C:N ratio ~3:1 after 24 cycles.
- **TDS** reveals sizeable shift of H_2O desorption temperature.

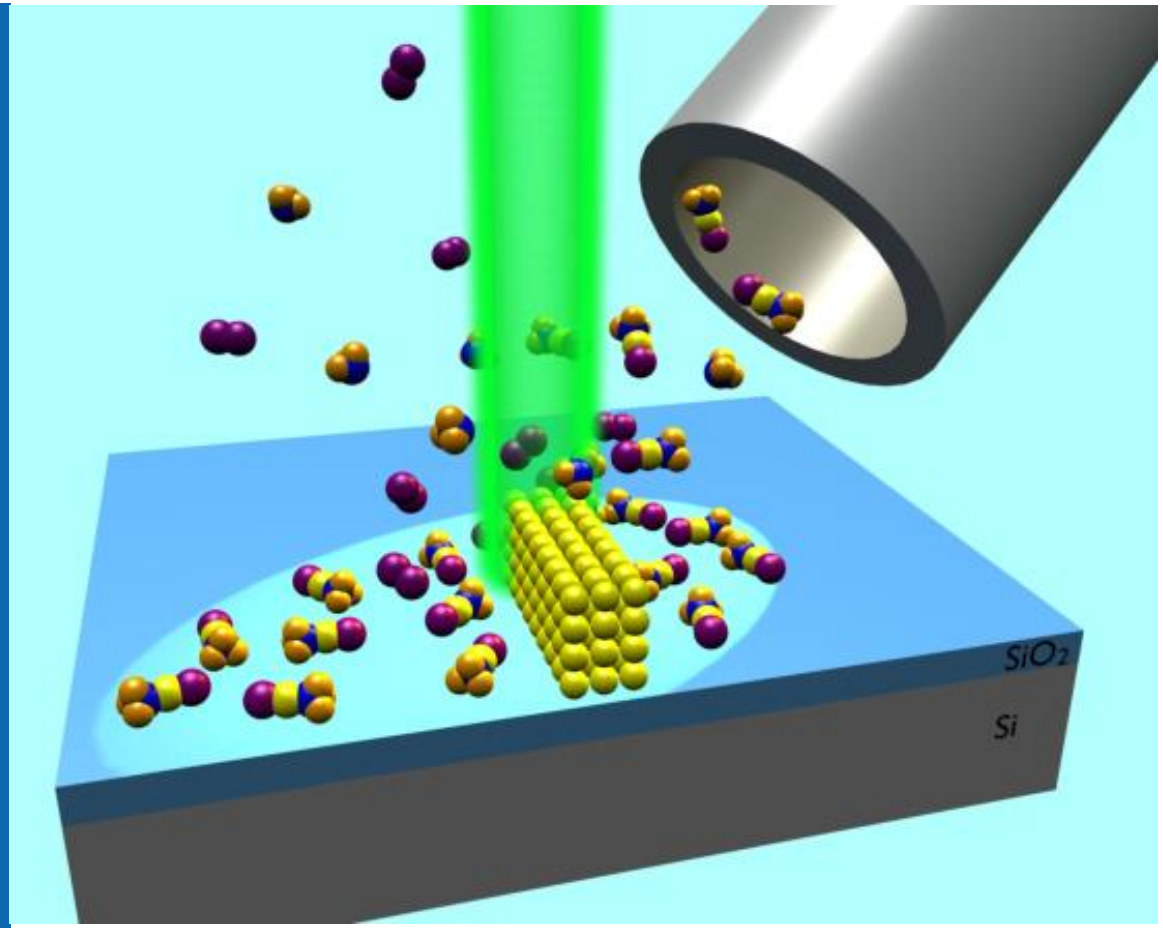


Deposit composition

H_2O desorption temperature



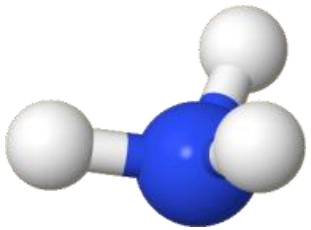
H. Boeckers, P. Swiderek, M. Rohdenburg, *Nanomaterials* **12**, 4455 (2022).



Chemistry of electron-induced nanofabrication

- Focused electron beam induced deposition (FEBID)
- Extreme ultraviolet lithography (EUVL)

Electron-driven nanofabrication



- NH_3 in focused electron beam induced deposition (FEBID)
- Control of thermal Fe deposition from $Fe(CO)_5$ by NH_3
- Role of low-energy electrons in EUVL

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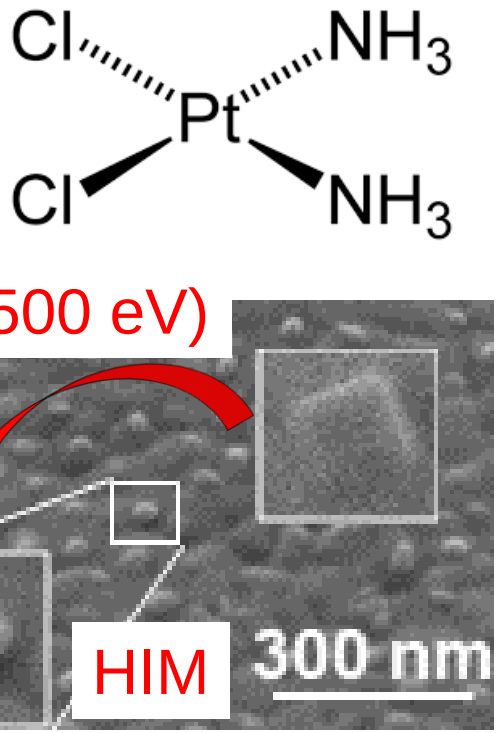
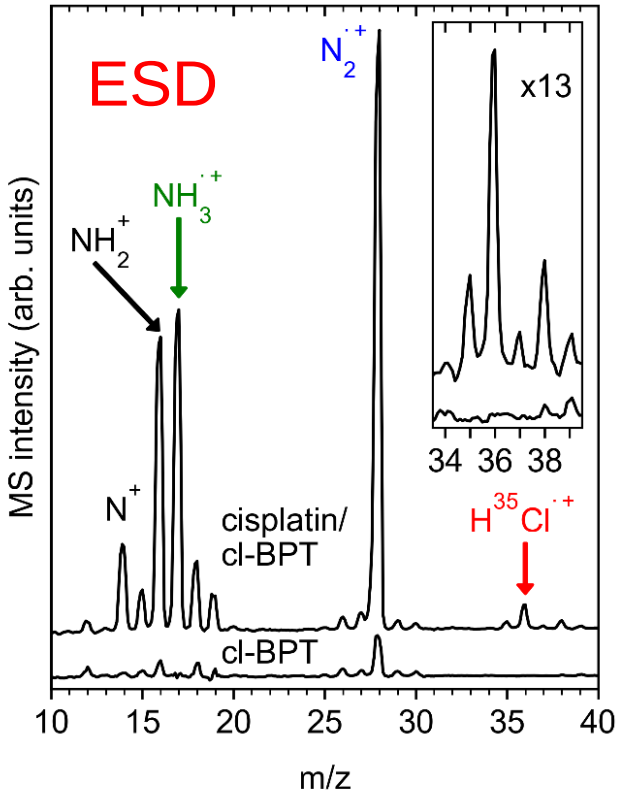
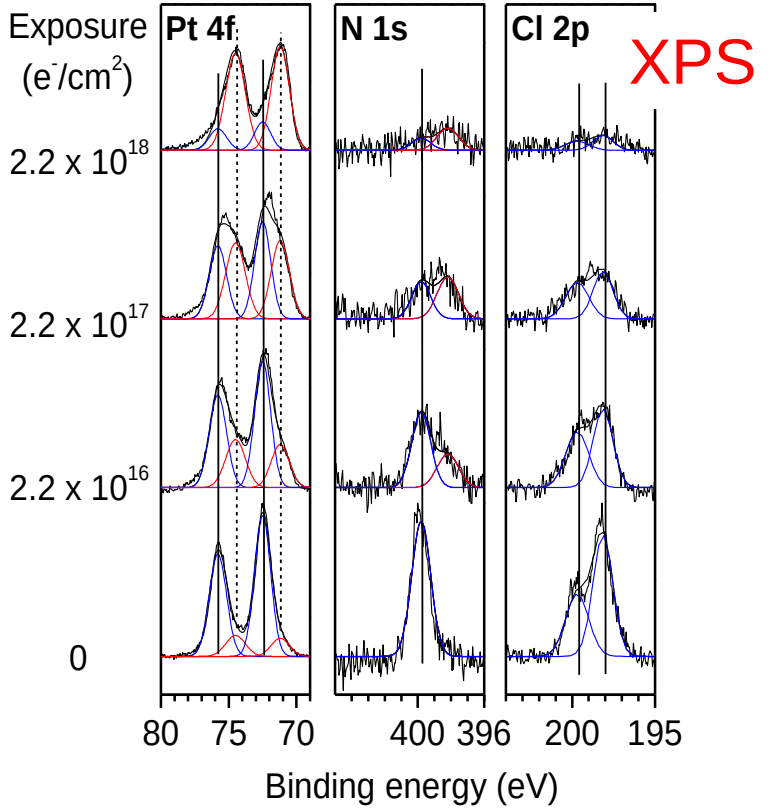
Cisplatin as FEBID precursor





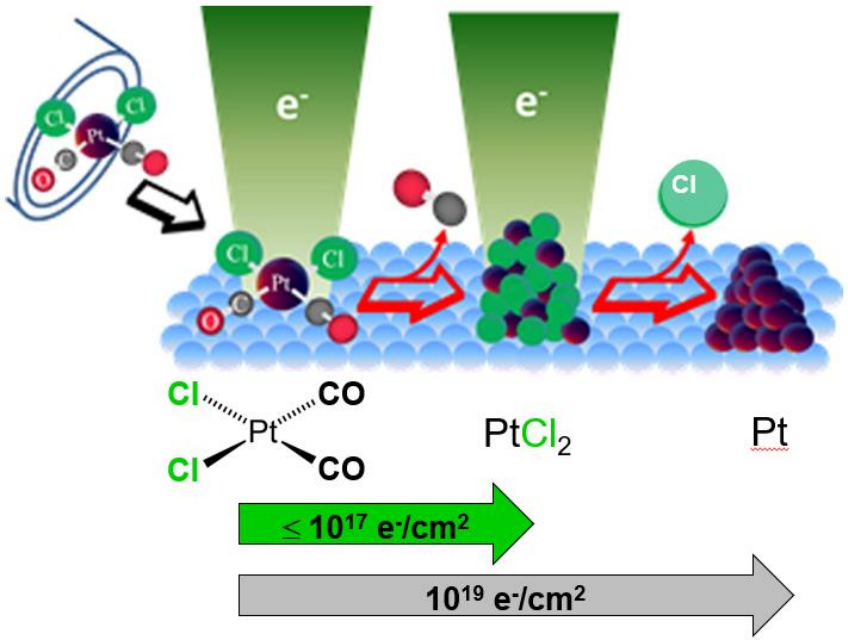


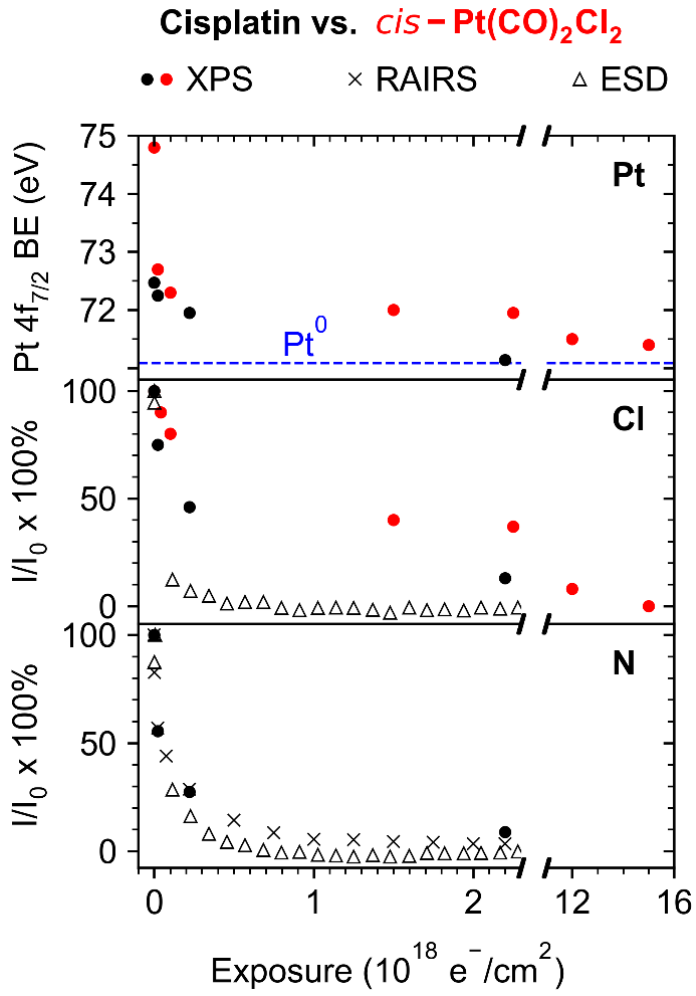
M. Rohdenburg, P. Martinović, K. Ahlenhoff, S. Koch, D. Emmrich, A. Gölzhäuser, P. Swiderek, *J. Phys. Chem. C* **123**, 21774 (2019).

Cisplatin versus $Pt(CO)_2Cl_2$

- Rapid loss of CO.
- Slow removal of Cl.

- NH_3 enhances loss of Cl and reduction to Pt(0).





J. A. Spencer, Y.-C. Wu, L. McElwee-White, D.H. Fairbrother, *J. Am. Chem. Soc.* **138**, 9172 (2016).
M. Rohdenburg, P. Martinović, K. Ahlenhoff, S. Koch, D. Emmrich, A. Gölzhäuser, P. Swiderek, *J. Phys. Chem. C* **123**, 21774 (2019).

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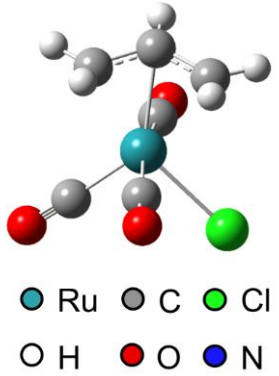
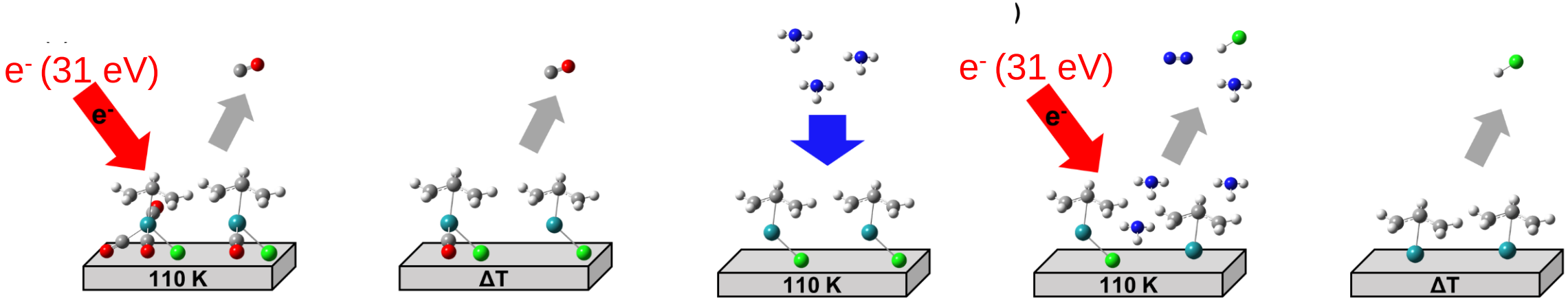
$(\eta^3\text{-}C_3H_5)Ru(CO)_3Cl$

η^3-allyl ruthenium tricarbonyl chloride



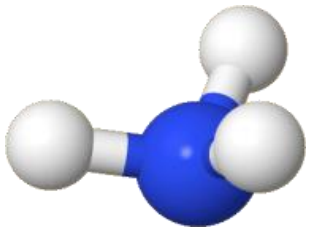
Deposit prepared by electron irradiation of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Cl$

NH_3-assisted removal of Cl.



M. Rohdenburg, **H. Boeckers**, C. R. Brewer, L. McElwee-White, P. Swiderek, *Sci. Rep.* **10**, 10901 (2020).

Electron-driven nanofabrication



- NH_3 in focused electron beam induced deposition (FEBID)
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- Role of low-energy electrons in EUVL

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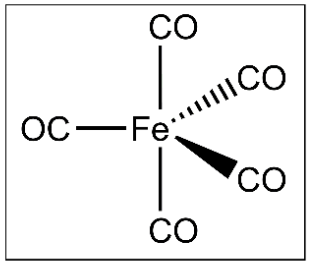
Use of NH_3 to control thermal reactions

- In UHV, $Fe(CO)_5$ supports autocatalytic growth of Fe.
- NH_3 inhibits Fe growth.
- Electron irradiation removes NH_3 and reactivates Fe growth.



Iron pentacarbonyl

P. Martinović, L. Barnewitz, M. Rohdenburg, P. Swiderek, *J. Vac. Sci. Technol. A* **41**, 033207 (2023).

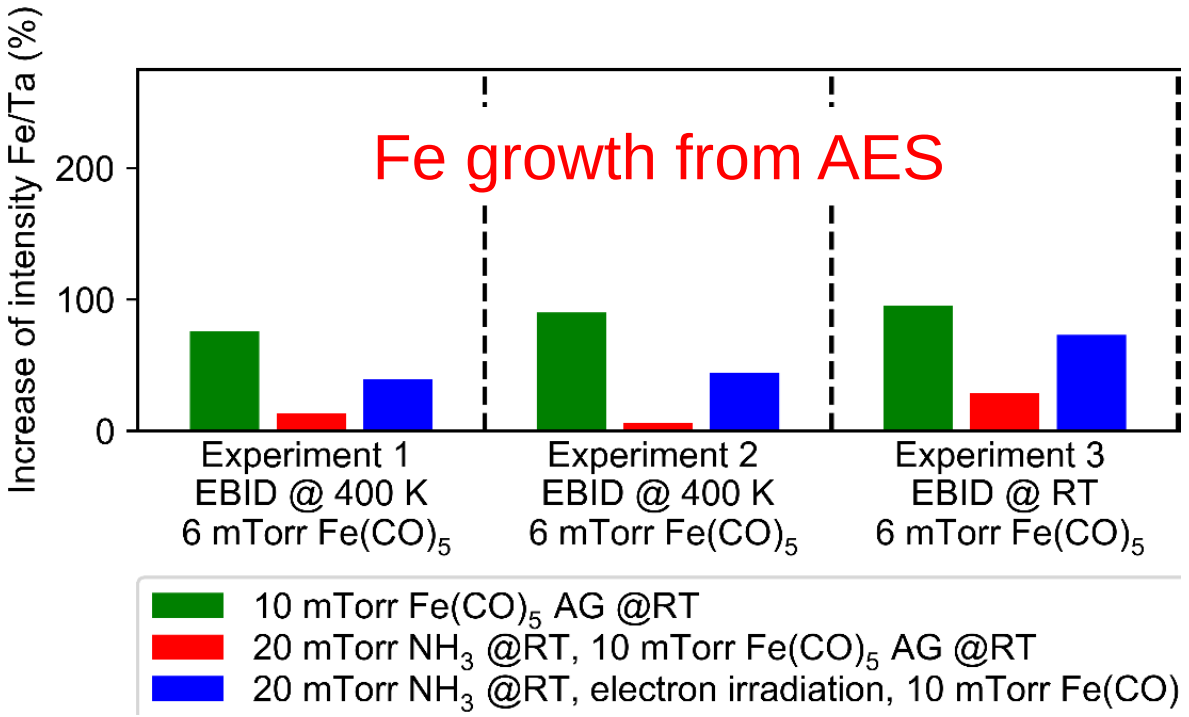
Use of NH_3 to control thermal reactions

Comparison of Fe growth

- on deposit prepared by EBID (green),
- on the same deposit after adsorption of NH_3,

and

- on the same deposit after adsorption of NH_3 and subsequent electron exposure.



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Electron-driven nanofabrication

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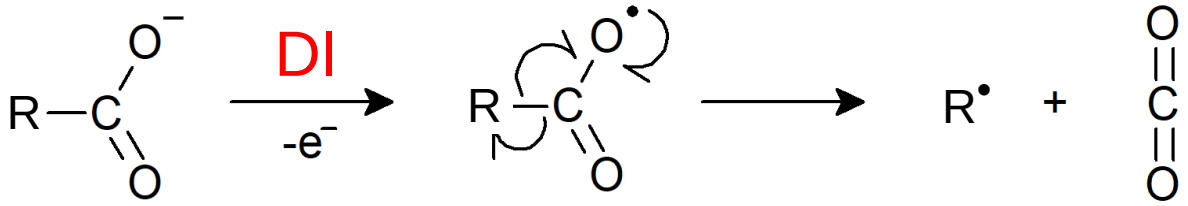
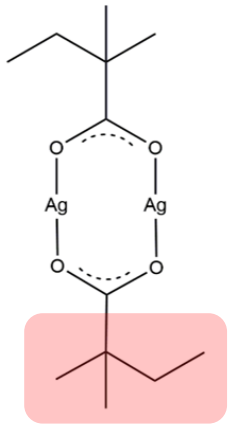
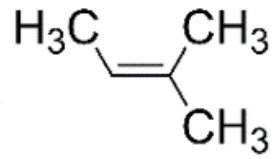
Related chemistry of FEBID and EUVL

Loss of CO_2 drives fragmentation of carboxylates. This is exploited both in FEBID and in EUVL.



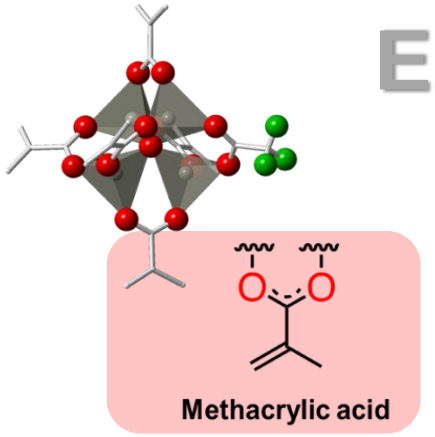


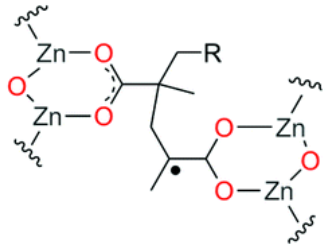
FEBID



P. Martinović et al.
Nanomaterials **12**, 1687 (2022).

EUVL





M. Rohdenburg, N. Thakur et al.,
Phys. Chem. Chem. Phys. **23**, 16646-16657 (2021).

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Thank you for your attention !

Deutsche Forschungsgemeinschaft DFG

DAAD Deutscher Akademischer Austausch Dienst German Academic Exchange Service

ELENA

CELINA